# Multiparticle exciton-impurity complexes in silicon in a magnetic field

V. D. Kulakovskiĭ, A. V. Malyavkin, and V. B. Timofeev

*Institute of Solid State Physics, USSR Academy of Sciences*
(Submitted 10 July 1978)
Zh. Eksp. Teor. Fiz. **76**, 272–287 (January 1979)

The Zeeman splitting in the emission spectra of multiparticle exciton-impurity complexes ($E_m$IC) on donor (phosphorus) and acceptor (boron) impurity centers is investigated, and the shell structure of the $E_m$IC is confirmed. The electronic states of the complexes in a magnetic field are classified by the values of the projections of the angular momenta in the electron and hole shells. The restructuring of the complexes under conditions when the valence-band degeneracy is lifted with the aid of uniaxial deformations is analyzed. The $g$ factors of the electrons and holes are determined. The diamagnetic shift in the emission spectra of the $E_m$IC is investigated and the dimensions of the complexes are estimated.

PACS numbers: 71.35. + z, 71.70.Ej, 71.55.Dp

## 1. INTRODUCTION

The emission spectra of indirect semiconductors that contain weakly coupled centers of the donor or acceptor type acquire, at sufficiently high excitation densities and low temperatures, a number of narrow lines. This line structure was first observed in the recombination spectra of silicon doped with boron, and was interpreted as the result of emission of excitons or of electron—hole pairs ($E$-$H$ pairs) in a multiparticle exciton-impurity complex ($E_m$IC), where $m$ is the number of excitons or pairs connected with the center.[1]

Considerable progress in the understanding of the internal structure of such complexes was made following the work by Kirczenow,[2] who proposed a shell model (SM) that recalls in many aspects the shell structure of multielectron atoms. According to this model, the electrons and holes in a multiparticle complex fill in succession the shells in accordance with the Pauli principle. It follows from the SM that strongly coupled $E_m$IC (with $m > 1$) are produced only in semiconductors with degenerate bands. Because of the band degeneracy, the number of single-particle electronic states in the complex, which are characterized by the principal quantum number, increases in accordance with the degeneracy multiplicity.[1)] The shell model classifies the electron (hole) states of the complex by the symmetry type, predicts the number of lines in the radiative-recombination spectra and their fine structure. For example, within the framework of the SM it is possible to describe well the singularities of the $E_m$IC spectra in Si in the absence of external actions,[4,5] and also in uniaxially deformed crystals.[6] In particular, direct experiments under conditions of uniaxial compression in Si have demonstrated[6] that band degeneracy is a necessary condition for the formation of $E_m$IC (see also Ref. 7).

One of the direct ways of verifying the SM is to investigate the $E_m$IC spectra in a magnetic field. This in fact is the main content of the present paper. In accordance with the character of the Zeeman splitting it is possible to classify the electronic states of the complexes by the values of the projections of the angular momenta in the electron and hole shells. It has turned out that is is preferable to compare the Zeeman spectra of the $E_m$IC with the splitting picture that follows from the SM premises, when the spin-excited states are not populated ($g\mu H \gg kT$). In Sec. 2 we describe the experimental procedure. The Zeeman splitting in the $E_m$IC spectra on a neutral donor in undeformed and uniaxially deformed Si(P) crystals are analyzed in Secs. 3 and 4, respectively.[2)] The influence of the magnetic field on the spectra of the multiparticle complexes on acceptor centers in Si(B) is investigated in Sec. 5. In Sec. 6, finally, we study the diamagnetic shift in the $E_m$IC spectra in Si(P) and Si(B) and estimate the linear dimensions of the complexes.

## 2. EXPERIMENTAL TECHNIQUE AND CRYSTALS

We used for the investigations silicon single crystals doped with shallow substitutional impurities, namely, Si(P) with phosphorus donor atom concentration $2 \times 10^{14}$ cm$^{-3}$, and Si(B) with boron atom concentration $10^{15}$ cm$^{-3}$. The samples were cut in the form of rectangular plates with linear dimensions $1.5 \times 3 \times 10$ mm in such a way that the longest edge was parallel to the ⟨111⟩ crystallographic direction. The accuracy of the crystallographic orientation was not worse than 1°.

To produce a homogeneous elastic deformation we used the device shown in Fig. 1. The sample 4 was placed between parallel planes of plungers 2, made of brass and having a diameter 15 mm. The plungers could be moved freely inside a cylindrical frame 1. The lower plunger was fixed with the aid of a faceplate.

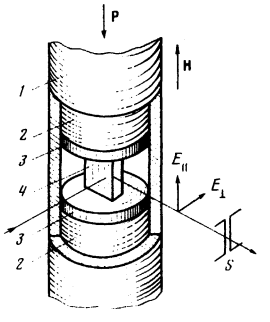


FIG. 1. Setup for the production of homogeneous deformation. The directions of the exciting laser beam, and of the polarization, in which the spectra were recorded, are indicated; $S$—entrance slit of monochromator.

 0038-5646/79/010139-08$02.40  

The applied force $P$ was parallel to the axis of the frame and was transmitted through the upper plunger to the sample in the direction of the longest edge. Linears of lead-tin alloy, about 1.5 mm thick, were placed between the crystal and the plungers. A small pressure was applied first at room temperature, so that the sample was slightly pressed into the liners (~0.5 mm). The sample was then cooled to helium temperature. It was then possible to deform the samples to pressures of several kilobars. Under the experimental conditions, the homogeneity of the deformation was high, as monitored against the width of the lines of the exciton-impurity complexes under conditions of surface and volume excitation. At a spectral resolution of approximately 0.1 meV, we did not notice any inhomogeneous broadening of the EIC lines up to uniaxial pressures of 2–3 kbar.

The device for the production of the elastic deformation was placed together with the sample inside a superconducting solenoid that ensured a sufficiently high aperture of the installation (1:7). The directions of the magnetic field and of the compression axes of the samples coincided under the experimental conditions. The homogeneity of the magnetic field was not worse than $10^{-4}$ inside the volume occupied by the sample. The accuracy of the orientation of the samples along the direction of the magnetic field was approximately 3°. The work was carried out in fields up to 80 kOe. The superconducting solenoid, the device for the deformations, and the sample were in superfluid helium at $T = 1.8$ K.

The nonequilibrium carriers were excited with the aid of a cw argon laser of 0.5 W power. The recombination radiation was registered with a photomultiplier cooled to $T = -60$°C and having an S-1 cathode. The photomultiplier operated in the photon-counting regime, so that the sensitivity of the photoelectric registration system was about $10^{-14}$ W. The spectral instrument was a large-aperture double monochromator with a dispersion 10 Å/mm in the working region.

## 3. ZEEMAN SPLITTING IN EMISSION SPECTRA ON A NEUTRAL DONOR IN Si(P)

1. *Structure of* $E_m$IC *on a donor within the framework of the shell model.* Silicon is an indirect semiconductor and contains six equivalent electron valleys, so that according to the effective-mass approximation, the first 1$s$ state of the electron in a weakly bound substitutional donor center should be 12-fold degenerate. However, since the potential of the impurity has a lower symmetry ($T_d$) than the crystal ($O_h$), this state, with allowance for the valley-orbit interaction, is split into a free symmetrical state $\Gamma_1$ and states antisymmetrical with respect to the valleys $\Gamma_3$ and $\Gamma_5$, with respective degeneracy multiplicities 2, 4, and 6 with allowance for the spin.[9]

In the ground state of a single exciton-impurity complex on a neutral donor ($E_1$IC) in Si, two electrons occupy a singlet state $\Gamma_1(1/2, -1/2)$ which is symmetrical with respect to the valleys. The wave function of the hole has the symmetry of the valence band $\Gamma_8$ and belongs to a fourfold degenerate state with angular momentum $j = 3/2$ (Ref. 10).

According to the shell model[2] for $E_m$IC ($m > 1$), with increasing number of $e$-$h$ pairs in the complex the additional holes occupy single-particle states $\Gamma_8$ until this shell becomes fully filled with four holes. Since the electron shell $\Gamma_1$ can contain only two electrons, the next electrons that enter the complex occupy the nearest 1$s$ state $\Gamma_3$ or $\Gamma_5$. Since the $\Gamma_3$–$\Gamma_5$ splitting is much less than $\Gamma_1$–$\Gamma_3$, these states will henceforth be designated $\Gamma_{3,5}$. They can contain ten electrons. Within the framework of the SM, the ground states of the $E_m$IC on a donor with $m \leq 4$ are $\{2\Gamma_1, (m-1)\Gamma_{3,5}; m\Gamma_8\}$, and the nearest excited states are $\{\Gamma_1, m\Gamma_{3,5}; m\Gamma_8\}$, i.e., states in which one electron from the shell $\Gamma_1$ goes over into $\Gamma_{3,5}$. Thus, the shell model classifies in a definite manner the electronic states of the complexes by symmetry type, and by the same token predicts the number of lines in the recombination spectrum and their fine structure. A direct check on the reliability of this classification consists of investigating the $E_m$IC spectra in a magnetic field.

The most convenient for investigations of the multiplet splitting in a magnetic field turned out to be the zero-phonon lines corresponding to processes of recombination with transfer of the excess quasimomentum to the crystal defect. These lines have as a rule a width smaller than 0.1 meV. The probability of the zero-phonon transitions is determined by the overlap integral of the wave functions of the recombining particles on the impurity center. From among the single-electron wave functions $\Gamma_1$, $\Gamma_3$, and $\Gamma_5$, only the fully symmetrical wave function $\Gamma_1$ extends noticeably over the impurity site. Therefore in the zero-phonon region of the spectrum the predominant $E_m$IC emission lines are those corresponding to recombination of the $\Gamma_1$ electrons with holes of symmetry $\Gamma_8$ (the so-called $\alpha$ transitions). Thus, in the case of $\alpha$ transitions, as a result of the act of recombination with emission of a photon $h\nu$, the remaining complex $E_{m-1}$IC with $m > 1$ turns out to be in an excited state:

$$\{2\Gamma_1, (m-1)\Gamma_{3,5}; m\Gamma_8\} \rightarrow \{\Gamma_1, (m-1)\Gamma_{3,5}; (m-1)\Gamma_8\} + h\nu. \quad (1)$$

In a magnetic field, the electronic states of the $E_m$IC are split. If the $g$ factors of the $\Gamma_1$ electrons and $\Gamma_8$ holes in the multiparticle complex are the same as in the usual EIC, then according to the shell model the total number of Zeeman components for the lines $\alpha_1$–$\alpha_4$, with allowance for all the allowed transitions between the spin-split states, should remain constant.[2] This agrees with the experimental observations under conditions wherein $g\mu H \sim kT$ (Ref. 11). The intensity ratio of the Zeeman components should be determined by the rates of single-electron transitions between the corresponding spin sublevels (see Table I of Ref. 2).

Qualitative differences occur between the Zeeman spectra of $E_m$IC in the case when the spin-excited states of the $E_m$IC are not populated ($g\mu H \gg kT$). Because of the strong difference between the intensities of the Zeeman components under these conditions, it is possible to classify unambiguously the observed optical

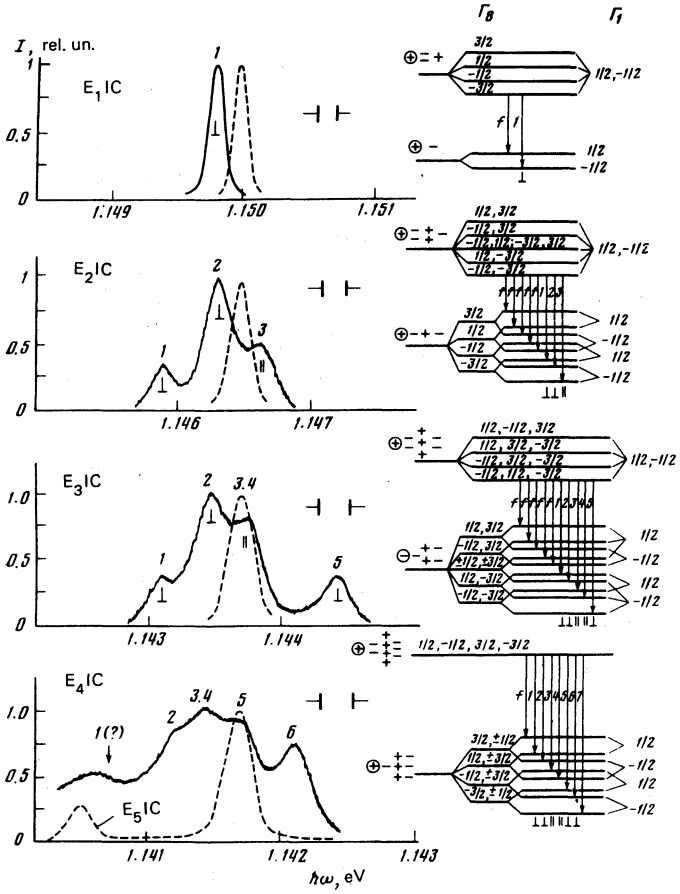


FIG. 2. Splitting of zero-phonon lines of $E_mIC$ radiation in undeformed Si(P) crystals at $T = 1.8$ K and $H = 62$ kOe, $\mathbf{H} \parallel \langle 111 \rangle$, and $\mathbf{H} \perp \mathbf{k}$. The dashed lines show the spectrum of the $E_mIC$ without the magnetic field. The radiation polarized parallel and perpendicular to H is marked by the symbols $\parallel$ and $\perp$. On the right are shown the schemes of the allowed optical transitions (the splitting of the $\Gamma_{3,5}$ shell, whose electrons do not participate in the recombination, is not shown).

transitions. In this case the number of allowed Zeeman components changes from one for the $\alpha_1$ line to six for the $\alpha_4$ line.

2. $E_mIC$ *spectra in* Si(P) *in a magnetic field.* Figure 2 shows the $E_mIC$ emission spectra ($\alpha_m$ lines, $m = 1$–$4$) in Si(P), measured in a magnetic field $H = 62$ kOe in the Voigt configuration ($\mathbf{H} \perp \mathbf{k}$) at $T = 1.8$ K. It is seen that the number of Zeeman components in the spectrum increases with increasing number of $e$-$h$ pairs in the complex. From a comparison of the picture of the splitting of the lines $\alpha_1$–$\alpha_4$ on Fig. 2 under the conditions $g\mu H \gg kT$ with the observed[11] picture at $g\mu H \sim kT$ it follows that the emission lines corresponding to recombination from excited spin sublevels vanish in the spectrum when the splitting between the sublevels greatly exceeds $kT$. The relative intensities of all the Zeeman components observed in Fig. 2 do not change when the field is increased from 40 to 80 kOe [$gH\mu \approx (3$–$6)kT$], and the spacing between the components increases linearly with $H$. This means that there is time for thermodynamic equilibrium to be established between the spin sublevels in $E_iIC$ in Si(P), and consequently the Zeeman spectra shown in Fig. 2 correspond to transitions from the state with the lowest spin (ground state). If we confine ourselves in the Hamiltonian of the interaction of the $E_iIC$ with the magnetic field to the terms that make the parametric contribution to the term splitting, then we can write for the energies of the states corresponding to definite values of the projections of the angular momenta of the electrons $S_z$ and of the holes $J_z$ in the $E_iIC$ complex

$$E^m(S_z, J_z) = E^m|_{H=0} + \mu H \left[ \sum_i g_i^e s_{zi} + \sum_k g_k^h j_{zk} \right], \qquad (2)$$

$$S_z = \sum_i s_{zi}, \quad J_z = \sum_k j_{zk},$$

where $g_i^e$ is the $g$ factor of the $i$-th electron with $z$-projection of the spin $s_{zi}$, and $g_k^h$ is the $g$ factor of the hole with the angular-momentum $z$-projection $j_{zk}$; the summation is over all the electrons with holes in the corresponding shells.

It must be borne in mind that the $g$ factors of the electrons in the shells $\Gamma_1$ and $\Gamma_{3,5}$ as well as of the holes with $j_z = \pm 3/2$ and $\pm 1/2$ are in the general case not equal to one another. The experimentally observed (Fig. 2) multiplet Zeeman splitting of the $\alpha_m$ lines can be explained if they are attributed to recombination of the electron from the filled $\Gamma_1$ shell having resultant electron spin equal to zero with the hole of $\Gamma_8$ in the ground spin state of the $E_iIC$. In this case the lowest spin state of the hole in the $E_iIC$ is characterized by an angular momentum projection $j_z = -3/2$. Therefore, in accordance with the selection rules listed in Table I, one component should be observed in the spectrum of the recombination of the $E_mIC$ in the magnetic field.

When the number of $e$-$h$ pairs in the $E_mIC$ is increased, the additional holes in the ground state of the complex, in accordance with the Pauli principle, occupy in succession states with angular momentum projections $j_z = -1/2$, $1/2$, and $3/2$. When the number of $e$-$h$ pairs in the complex is increased the number of allowed transitions increases in accordance with the selection rules.

Figure 2 shows the schemes of the expected transitions from the ground state of the $E_mIC$ to the spin-split $E_{m-1}IC$ states. The splitting of the shell $\Gamma_{3,5}$ is not shown on the transition scheme, since the electrons of this shell do not take part in the combination. It is seen from Fig. 2 that the experimentally observed number of Zeeman components in the $E_mIC$ lines and their state of polarization agrees sufficiently well with those expected in the framework of the SM. The emis-

TABLE I. Selection rules and relative probabilities of the radiative transitions between the spin sublevels in EIC*.

| | $j_z$ | | | |
|---|---|---|---|---|
| $s_z$ | $+3/2$ | $+1/2$ | $-1/2$ | $-3/2$ |
| $+1/2$ | 0 | $1/6X$, $1/6Y$ | $2/3Z$ | $1/2X$, $1/2Y$ |
| $-1/2$ | $1/2X$, $1/2Y$ | $2/3Z$ | $1/6X$, $1/6Y$ | 0 |

*$s_z$ and $j_z$ denote the respective projections of the electron spin and of the angular momentum of the hole; $X$, $Y$, $Z$—directions of polarization of the light, $z$—quantization axis.

sion lines corresponding to the transitions $\Delta(S_z+J_z)=0$ are not resolved in the spectra because of the close values of the $g$ factors for the electrons ($g_e$) and for the spin-1/2 holes ($g^h_{1/2}$). The component corresponding to the transition 1 is not resolved in the $E_4$IC spectrum, apparently because of the overlap with the unresolved structure of the Zeeman spectrum of the $E_5$IC complex.

Comparing the observed relative intensities of the Zeeman components with those calculated by Kirczenow[2] (Table I), we see that the discrepancy between them is large. To some degree these discrepancies are due to the depolarization of the radiation in the sample by uncontrollable multiple reflections. Thus, the degree of polarization of none of the investigated lines exceeded 30%. The reason for the difference between the relative intensities and the expected ones for identically polarized lines remains less clear.

3. *The g factors.* From the values of the splitting of the $\alpha$ lines in the magnetic field we can determine some of the $g$ factors for the $\Gamma_1$ electrons and $\Gamma_8$ holes in the excited states of the $E_m$IC. These results are given in Table II, which gives for comparison also the $g$ factors of the electrons and holes respectively on the neutral donor and acceptor. It follows from the table that on going from the neutral donor in $E_m$IC with $m = 1-3$, the change of $g_e$ does not exceed the experimental error (~5%). For the holes in EIC, the factors differ substantially from the $g$ factors of the holes on weakly bound acceptors.

Within the framework of the SM, for holes in $E_m$IC, just as in the case of a neutral acceptor, the Zeeman splitting is determined by a perturbation matrix $H_h$, which can be written, from symmetry considerations, in the form[12]

$$H_H=\mu\left[g_1\mathbf{JH}+g_2\sum_i J_i^3H_i\right], \tag{3}$$

where the coefficient $g_1$ determines the isotropy contribution to the $g$ factor, while $g_2$ determines the anisotropy correction. At $g_2=0$, the paramagnetic contributions to the energies of the states with $j_z=\pm1/2$ and $\pm3/2$ are the same and do not depend on the direction of the magnetic field $H$, i.e., $g^h_{1/2}=g^h_{3/2}$. In silicon, owing to the angular dependence of the wave function of the hole at the impurity center, the correction $g_2$ for the anisotropy differs from zero. At $g_2\neq0$, the Zeeman splitting depends on the orientation of the magnetic field and $g^h_{1/2}\neq g^h_{3/2}$. In the case $\mathbf{H}\parallel\langle111\rangle$

TABLE II. The $g$ factors of the bound electrons and holes in $E_m$IC in Si(P) for the direction $\mathbf{H}\parallel\langle111\rangle$.

| Sample | Number of e-h pairs in $E_m$IC | $g_e$ | $g^h_{1/2}$ | $g^h_{3/2}$ | $g^h_{3/2}-g^h_{1/2}$ | $g_1$ | $g_2$ |
|---|---|---|---|---|---|---|---|
| Si(P) | 3 | 1.9±0.1 | 1.8±0.2 | 1.2±0.2 | 0.6±0.2 | 0.6 | 0.4 |
| | 2 | 1.9±0.1 | 1.8±0.2 | – | – | | |
| | 1 | 2.0±0.1 | – | – | 0.6±0.2 | | |
| | 0* | 2.0 [19] | – | – | – | | |
| Si(B) | 0** | – | 1.45 [20] | 1.1 [20] | | 1.03 [20] | 0.04 [20] |

*Neutral donor.
**Neutral acceptor.

(Ref. 12) we have

$$g^h_{1/2}=g_1+{}^{13}/_4 g_2,$$
$$g^h_{3/2}={}^1/_3[6(g_1+{}^9/_4 g_2)^2+3(g_1+{}^5/_4 g_2)^2]^{1/2}. \tag{4}$$

From the data of Table II we see that the difference $g^h_{3/2}-g^h_{1/2}$ in $E_m$IC does not change when the number of holes in the $\Gamma_8$ shell is increased, but it is much larger than the corresponding $g$-factor difference for a hole in a neutral acceptor. This means apparently that the angular dependence of the $g$ factor for the holes of $\Gamma_8$ in a multiparticle complex is much stronger than in the case of a neutral acceptor. This difference between the wave functions of the holes of $\Gamma_8$ in $E_m$IC and in a neutral acceptor seems natural to us and depends on the degree of deviation of the impurity potential from spherical symmetry. Whereas in an acceptor the deviation of the potential from spherical symmetry is most significant within the limits of the unit cell of the crystal, in the complex, owing to the $\Gamma_1$ electrons, this difference can extend over distances of the order of the Bohr radius for the $\Gamma_1$ electron.

It should also be noted that, owing to the close values of the effective masses of the electrons and holes, the dimensions of the $\Gamma_1$ and $\Gamma_8$ shells should be comparable.

Using the obtained values of $g^h_{1/2}$ and $g^h_{3/2}$ we obtain for $E_m$IC with the aid of (4) that $g_1=0.6$ and $g_2=0.4$.

The spectral shift $\Delta\alpha_m$ of the emission lines corresponding to transitions between the ground spin states relative to the $\alpha$ lines in the absence of a magnetic field is determined, as follows from (2), as follows:

$$\Delta\alpha_m={}^1/_2\beta_m\mu H, \tag{5}$$

where

$$\beta_1=g_e-3g^h_{3/2},\quad \beta_2=-g^h_{1/2}+g_e,\quad \beta_3=g_e+g^h_{1/2},\quad \beta_4=g_e+3g^h_{3/2}.$$

The difference between the measured and calculated values of $\Delta\alpha(1)$ at $H=80$ kOe does not exceed 0.15 meV, which is much less than $g_{e,h}\mu H$. This difference is due to the difference between the diamagnetic shifts in the initial and final states of the complex (see Sec. 6).

## 4. ZEEMAN SPLITTING IN THE $E_m$ IC SPECTRA IN UNIAXIALLY DEFORMED Si(P)

Uniaxial elastic deformations lift the degeneracy of the valence band. In the 1$s$ state, a nondegenerate valence band can contain not more than two holes. Therefore complexes containing not more than two electron-hole pairs remain stable in such crystals. When silicon is compressed along the $\langle111\rangle$ crystallographic direction, the structure of the conduction band, and consequently also of the electron shells in the complex, remains unchanged. The holes fill in this case the doubly spin degenerate shell $\Gamma_4$ (Ref. 2). The expected resultant splitting of the $E_m$IC terms at the neutral donor in a magnetic field, and also the zero-phonon transitions and the character of their polarization, are shown in Fig. 3. We have left out from the level scheme the splitting corresponding to the electron shell $\Gamma_{3,5}$, since the electrons of this shell do not take

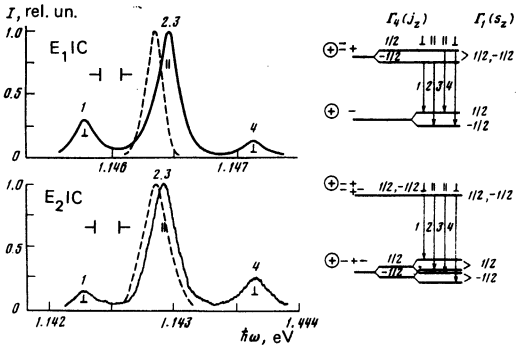


FIG. 3. Splitting of zero-phonon lines of the radiation of $E_mIC$ in deformed Si(P) crystals at $T=1.8$ K, $H=62$ kOe kg/mm$^2$. The dashed lines show the $E_mIC$ spectrum at $\mathbf{H}\|\langle 111\rangle$, $\mathbf{P}\|\mathbf{H}$, $P=23$ kg/mm$^2$. On the right are shown the schemes of the allowed optical transitions.

part in the recombination.

It follows from Fig. 3 that the total number of the transitions that are allowed in accordance with the selection rules for $E_1IC$ and $E_2IC$ is the same and equal to four. In the $E_1IC$, two transitions take place from the ground state and from the spin-unsplit state, since the shells $\Gamma_1$ and $\Gamma_4$ are completely filled, and the resultant angular momentum in them is therefore zero. Next, it is easy to obtain for the $g$-factor of the holes in the configuration $\mathbf{H}\|\mathbf{P}\|\langle 111\rangle$ the value[12] $g_{\|}^{h}=g_1+13/4g_2=1.9$. This value coincides with the $g$ factor of the $\Gamma_1$ electrons, so that the Zeeman components corresponding to transitions 2 and 3 should coincide in the spectrum.

The emission spectra of $E_mIC$ in an Si(P) crystal deformed along the $\langle 111\rangle$ axis and placed in a magnetic field $\mathbf{H}\|\mathbf{P}$ of 62 kOe are shown in Fig. 3. The spectra were measured in the Voigt configuration $\mathbf{H}\perp\mathbf{k}$. As expected, the $E_1IC$ and $E_2IC$ lines are split in a magnetic field into triplets. In the case of $E_1IC$, the intensity of component 4 decreases with increasing $H$ (transition from a spin-excited state). At the same time in $E_2IC$ the relative intensities of the Zeeman components remain unchanged. From the magnitude of the splitting it is easy to find that $g_e=g_{\|}^{h}=1.9\pm0.1$. These values of the $g$ factors are the same in $E_1IC$ and $E_2IC$. The polarization of individual components also agrees with that expected within the framework of the SM. Thus, results obtained under conditions of uniaxial compression confirm the SM. To conclude this paragraph, we finally call attention to the fact that the ratio of the intensities of the Zeeman component 4 and 1 in $E_1IC$ exceeds noticeably the value expected under conditions of quasiequilibrium between the spin sublevels. It follows therefore that the time of the spin relaxation in $E_1IC$ in deformed Si(P) crystals is at least larger than the lifetime of the complex ($\sim10^{-7}$ sec). Such an appreciable increase of the time of the spin relaxation in $E_1IC$ in deformed crystals of silicon is explained by the lifting of the degeneracy of the valence band.[13]

## 5. EMISSION SPECTRA OF $E_m$ IC AT A NEUTRAL ACCEPTOR IN A MAGNETIC FIELD IN Si(B)

The electron structure of multiparticle complexes at acceptor centers differs substantially from that of the $E_mIC$ on donors considered above. First, in such complexes there is a much stronger interaction of the angular momenta of the holes, the so called $j$-$j$ interaction, which is accompanied by additional splitting of the hole terms. This splitting is larger the stronger the binding of the acceptor.[4,14,15] Another still unanswered question is how large a splitting of the electron orbitals is produced by valley-orbit interaction in such complexes. It is therefore not clear beforehand how the electron shells become filled when the $e$-$h$ pairs are successively joined into complexes. For example, some authors[16] explain the experimentally observed degree of circular polarization of $E_2IC$ in Si(B) by assuming that the lowest electronic state, just as in Si(P), is the spin singlet $\Gamma_1$. There is, however, another point of view, according to which the valley-orbit splitting in $E_mIC$ on an acceptor is assumed to be small,[2,15] so that the electrons in such complexes are outside the central cell because of the repulsion potential produced by the negatively charged ion. This is confirmed by investigations of the influence of uniaxial deformation along the $\langle 100\rangle$ axis on the formation of $E_mIC$ on an acceptor,[6] which have established that in Si(B) the term splitting is $\Gamma_{3,5}-\Gamma_1<0.3$ meV, whereas in Si(P) $\Gamma_{3,5}-\Gamma_1=4$ meV. If in the case of interest to us the valley-orbit splitting turns out to be negligibly small, then the deepest electron shell in $E_mIC$ will have a higher degeneracy multiplicity than the quadruply degenerate lowest hole shell $\Gamma_8$.

An answer to these questions can be obtained with the aid of an analysis of the Zeeman splitting in the emission spectra of $E_mIC$. The acceptors used in the Si crystals were boron atoms, for which the $j$-$j$ interaction is relatively small and becomes smaller than the paramagnetic splitting of the terms $H\geqslant 30$ kOe. The most convenient for the investigations turned out to be the narrow zero-phonon lines. In Si(B), however, their intensity is low and furthermore decreases (as does also the intensity of the lines with phonon emission) with increasing magnetic field. We succeeded in tracing the splitting of the zero-phonon lines of the $E_mIC$ radiation with a resolution 0.2 meV only in fields up to 60 kOe. At $H>60$ kOe we investigated more intense lines corresponding to recombination of $e$-$h$ pairs with emission of a $TO$ phonon. In such strong fields the paramagnetic splitting exceeds the halfwidth of these lines (~0.3 meV).

1. *Elastically deformed* Si(B) *crystals.* We discuss first the spectra of the complexes in Si(B) that is elastically compressed along the $\langle 111\rangle$ axis. The electron structure of the EIC under these conditions becomes noticeably simpler because of the lifting of the degeneracy in the valence band. In this case the holes fill the $\Gamma_4$ shell, which is doubly degenerate in spin, and therefore complexes with $e$-$h$ pairs $m>1$ turn out to be unstable.[6] In $E_1IC$, two holes form a state singlet in the spin, which is not resolved because of the $j$-$j$ interaction.

The emission spectrum of $E_1IC$ in a magnetic field of 80 kOe and at a deformation $\mathbf{P}\|\langle 111\rangle$ ($P=12.5$ kg/mm$^2$) is shown in Fig. 4. This figure shows also the radia-

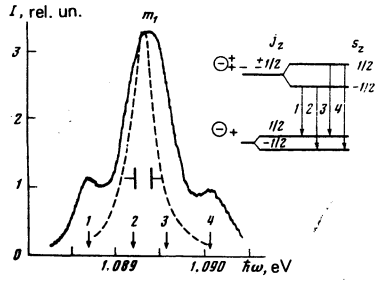


FIG. 4. Splitting of *TO* recombination line of $E_1IC$ in a deformed Si(B) crystal at $H = 80$ kOe and $P = 12.5$ kg/mm$^2$. The dashed line was obtained at $H = 0$; on the right is shown the scheme of the optical transitions.

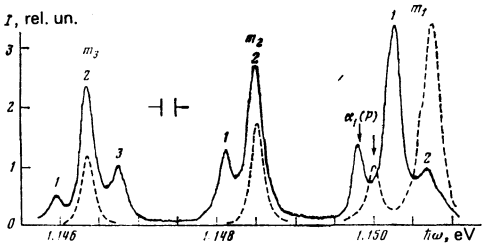


FIG. 5. Zero-phonon recombination spectrum of $E_mIC$ in Si(B) crystal in a magnetic field $H = 62$ kOe without deformation. The dashed line shows the $E_mIC$ spectrum at $H = 0$.

tive-transition scheme. Just as in deformed Si(P), the Zeeman components corresponding to transitions 2 and 3 are not resolved. However, the line corresponding to these transitions is noticeably broadened, so that the electron and hole $g$ factors $g_e$ and $g_h$ do not coincide.

By approximating the magnetic-field dependences of the $E_1IC$ levels and the acceptor with the aid of expression (1), we find that in $E_1IC$ $g_e + g_h = 3.1 \pm 0.2$, $g_e = 1.8 \pm 0.2$, $g_h = 1.3 \pm 0.2$ (Table III). The intensity distribution in the Zeeman emission spectrum in deformed Si(B) crystals indicates that, just as in elastically compressed crystals Si(P), the quasiequilibrium between the spin sublevels does not manage to set in within the lifetime of the complex (~$10^{-6}$ sec).

2. *Undeformed* Si(B) *crystals.* We shall now dwell on the singularities of the Zeeman emission spectra of $E_mIC$ on an acceptor in undeformed silicon crystals (Fig. 5). In a magnetic field $H = 62$ kOe and $T = 1.8$ K, the zero-phonon emission line $E_1IC$ ($m_1$) splits into a doublet. The spectrum of Fig. 5 shows also the line $\alpha_1$ connected with the residual impurity of the phosphorus atoms. With increasing magnetic field, the splitting between the components (1) and (2) of the $m_1$ line increases linearly, and the ratio of the intensity of the components (2) and (1) decreases ~$\exp[g^h \mu H/kT]$. This means, first, that the lifetime of the complex is sufficient for quasiequilibrium to become established between the spin sublevels in the undeformed Si(B) crystals and, second, that only the component (1) corresponds to a transition from the ground state of $E_1IC$. A substantial contribution to the ratio of the intensities of the components (1) and (2) is made by the pre-exponential factor, which is connected with the difference between the matrix elements of the transitions corresponding to these lines.

Figure 6 shows the scheme of the allowed transitions from the ground and nearest excited level in $E_1IC$. For transitions 1 and 3 the energies of the emitted photons coincide. The rates of the single-electron transitions 1 and 3 are smaller by a factor 4 than the probability of the transition 2, in good agreement with experiment.

Figure 5 shows the Zeeman spectra of the emission lines of $E_2IC$ ($m_2$) and $E_3IC$ ($m_3$), measured in the Voigt configuration in a field $H = 62$ kOe ($H \| \langle 111 \rangle$). The line $m_2$ splits into a doublet, and $m_3$ into a triplet. The relative intensities of the components remain unchanged within the limits of each multiplet when the magnetic field is increased from 40 to 80 kOe, and therefore all the components correspond to transitions from the ground state. To explain the observed splitting picture it must be assumed that in a magnetic field the ground state with two electrons in $E_2IC$ has a resultant angular-momentum projection $J_z = -1$, and for three electrons in $E_3IC$ in the ground state we have $J_z = -3/2$. If the two electrons in $E_2IC$ were to produce a spin singlet

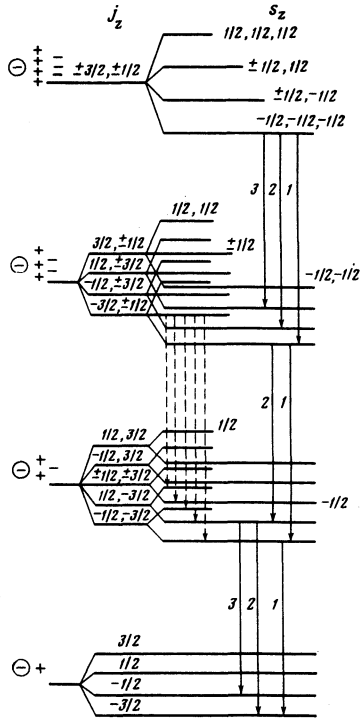


FIG. 6. Diagram of the allowed transitions, shown in Fig. 5, in a magnetic field. The Zeeman levels corresponding to different projections of the total spins of the electrons $S_z$ are designated by lines with different lengths. The dashed lines mark the transitions in the case when the two electrons in the $E_2IC$ form a spin singlet in the state of lowest energy.

TABLE III. The $g$ factors of bound electrons and holes in $E_mIC$ in Si(B) that is not deformed and is deformed along $P \| \langle 111 \rangle$ ($H \| \langle 111 \rangle$).

| Direction of deformation in Si(B) | Number of e-h pairs in $E_mIC$ | $g_e$ | $g^h_{1/2}$ | $g^h_{1/2} - g^h_{3/2}$ | $g^h_\|$ |
|---|---|---|---|---|---|
| No deformation | 2 | 1.85±0.1 | 1.2±0.1 | 0.2 | – |
| " | 1 | 1.85±0.1 | 1.2±0.1 | 0.2 | – |
| $P \| \langle 111 \rangle$ | 1 | 1.85±0.1 | – | – | 1.3±0.1 |

$\Gamma_1$, then, for example, the $m_2$ line would be split in the magnetic field into a quintet (such a splitting is shown dashed on the scheme of Fig. 6), something not observed in experiment. Thus, the state $\Gamma_1$ is not the ground state for the electrons in complexes on a neutral acceptor. The observed spectra of the multiplet splitting of the lines $m_2$ and $m_3$ in a magnetic field are explained by the schemes of the optical transitions in Fig. 6.

From the value of the Zeeman splitting we can determine the $g$-factors of the holes in the complexes. The obtained values for the $g$-factors are shown in Table III. In undeformed Si(B) at $H \| \langle 111 \rangle$ $g^{h}_{1/2} \approx g^{h}_{3/2}$, and these quantities agree well with the $g$ factors for the holes in a neutral acceptor. It follows therefore that in complexes with a neutral acceptor, in contrast to $E_m$IC in Si(P), the wave functions for the holes have, not unexpectedly, a weak angular dependence. It was noted above that the strong angular dependence of the wave functions of the holes in the $E_m$IC in Si(P) is due in all probability to the deviation of the symmetry of the wave functions of the electrons from spherical, a deviation which is largest for the $\Gamma_1$ electrons. In the case of $E_m$IC in Si(B), the anisotropic increment to the $g$-factor for the holes should be small.

In concluding this section we note that the $g$-factor of the electrons in the complexes can be determined by measuring the energy changes of the emitted photons in transitions from the ground state of the $E_m$IC to the ground state of $E_{m-1}$IC. For this change we can write

$$\Delta\hbar\omega_m = {}^1/_2\beta_m\mu H,$$

where

$$\beta_1 = -{}^1/_2(g_e + g^{h}_{1/2}), \quad \beta_2 = -g_e + g^{h}_{1/2}, \quad \beta_3 = -g_e + 3g^{h}_{1/2}.$$

It follows from experiment that $g_e = 1.8 \pm 0.2$ for all the $E_m$IC in Si(B).

## 6. DYNAMIC SHIFT IN THE EMISSION SPECTRA OF MULTIPARTICLE COMPLEXES

Figures 7 and 8 show the dependences of the positions, on the energy scale, of the Zeeman components in the

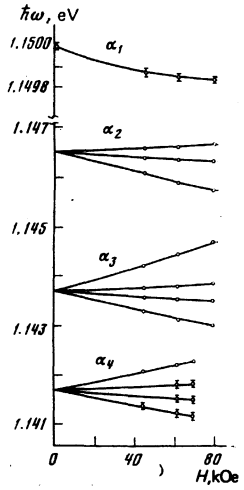


FIG. 7. Dependence of the energy position of the Zeeman components of the $\alpha$ lines in the luminescence spectrum of Si(P) on the magnetic field.

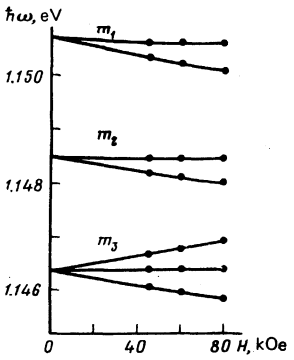


FIG. 8. Magnetic-field dependence of the position of the Zeeman components of the $E_m$IC line in the spectrum of Si(B).

emission spectra of multiparticle complexes with donor and acceptor impurities on the magnetic field. In first-order approximation these dependences are described by terms that are linear in $H$ in the Hamiltonian of the interaction of the $E_m$IC with the magnetic field. However, even in fields $H > 50$ kOe noticeable discrepancies are observed between the linear approximations and the experimental observations. By way of example, this is illustrated in an enlarged scale for the $\alpha_1$ line of $E_1$IC in Si(P) in Fig. 7.

The measured dependences can be described more accurately by including in the expression for the spectral shift a term quadratic in the magnetic field

$$\hbar\omega(\alpha_m)|_H = \hbar\omega(\alpha_m)|_{H=0} + \beta_m H + \gamma_m H^2. \tag{6}$$

It turned out that the values of $\gamma_1$ for $E_1$IC in Si(P) and Si(B) practically coincide and agree well with the values of $\gamma_1$ for $E_1$IC in Si(As), as obtained in Ref. 10.

The term of (6) quadratic in the magnetic field stems from the diamagnetic susceptibility of the complexes and is due to the difference between the diamagnetic shifts of the initial and final states:

$$\gamma_m H^2 = \Delta E^{\text{dia}}_m - \Delta E^{\text{dia}}_{m-1}. \tag{7}$$

For a quantitative description of the diamagnetic shift of the terms in $E_m$IC, we use the expression obtained for a multielectron atom in first-order perturbation theory[17]:

$$\Delta E^{\text{dia}}_m = \frac{e^2H^2}{12c^2}\sum_i \frac{\overline{r_i^2}}{m_i}, \tag{8}$$

where the summation is carried out over both the electron and hole states. For qualitative estimates we can assume that, just as for the 1$s$-hydrogenlike wave function, $\overline{r_i^2} = 3a_B^2$. For a neutral donor on phosphorus, the radius of the Bohr orbit of the electron is $a^e_B = 15$ Å and $\Delta E_0^{\text{dia}} = 0.3 \cdot 10^{-5} H^2$ (meV). From (7) we find that for an $E_1$IC with a donor

$$\Delta E_1^{\text{dia}} = \Delta E_0^{\text{dia}} + \gamma_1 H^2 \approx 2.2 \cdot 10^{-5} H^2 \text{ meV}.$$

If we use expression (8), we easily verify that even in the extreme case $a^e_B \gg a^h_B$ the dimension of the $E_1$IC does not exceed the Bohr radius of the exciton ($a^{ex}_B \approx 45$ Å). Inasmuch as $m_e \approx m_h$ in the complex, we can assume for estimates that $a^e_B \approx a^h_B$. We then get for the $E_1$IC radius $a^{EIC}_B \approx a^e_B \approx 0.65 a^{ex}_B$ (~30 Å). The quadratic shifts for the emission lines of $E_1$IC in Si(B) and Si(P)

TABLE IV. Values of $\gamma_m$ for the emission lines of $E_mIC$ in Si(P) and Si(B).

| Si(P) emission lines | $\gamma_m \cdot 10^5$ meV/kOe² | Si(B) emission lines | $\gamma_m \cdot 10^5$ meV/kOe² |
|---|---|---|---|
| $\alpha_1$ | 1.9 | $m_1$ | 2.3 |
| $\alpha_2$ | 2.5 | $m_2$ | 2.0 |
| $\alpha_3$ | 2.5 | $m_3$ | 0.5 |
| $\alpha_4$ | 0 | | |

agree within the limits of their errors (20%), so that the radius of the $E_1IC$ in Si(B) is equal to $E_B^{E_1IC} \approx a_B^e \approx 0.65\, a_B^{ex}$. The values of $\gamma_1$ for $E_mIC$ in Si(P) and Si(B) are listed in Table IV.

It is of particular interest to know how the dimension of the complex varies when the number of electron-hole pairs in it increases. In the case of $E_mIC$ with a neutral donor, unfortunately, it is impossible to determine the dimension of a complex with $m>1$ from only measurements of the diamagnetic shift of the $\alpha_m$ lines. The point is that the $\alpha_m$ lines at $m>1$ correspond to transitions to the excited states $E_{m-1}IC$, so that the contributions made to $\gamma_m H^2$ by the initial and final states cannot be separated.

These difficulties do not arise in the case of transitions between the ground states of the complex. Such a situation obtains in $E_mIC$ in Si(B). It follows from (7) and (6) that

$$\Delta E_m^{dia} = \Delta E_0^{dia} + \sum_{i=1}^{m} \gamma_i H^2.$$

Assuming $a_B^e \approx a_B^h$ and using (8), we find that the Bohr radii $E_2IC$ and $E_3IC$ in Si(B) are respectively (33 ± 5) Å and (28 ± 6) Å. These values agree well with a recent calculation.[18]

Thus, the dimension of a multiparticle complex with an acceptor center remains practically unchanged when the number of the $e$-$h$ pairs that are bound to this center increases, even if the hole shell becomes completely filled.

We regard these results as of interest. It follows from them that when the number of $e$-$h$ pairs in the complex increases, the electron-hole density increases. This should be accompanied by an increase of the correlation energy per particle, meaning of the binding energy of the multiparticle complex as a whole; this does not contradict the experimental observations. This tendency to "self-contraction" of the dimensions of the multiparticle complexes and to an increase of their stability should manifest itself when the number of particles increases within the limits of one shell (in particular, the hole shell) up to complete filling of the shell.

In conclusion the authors consider it their pleasant duty to thank G. E. Pikus, É. I. Rashba, and V. M. Édel'shtein for useful discussions of the content of the paper.

[1)] It was predicted earlier[3] that stable multiparticle free complexes can exist in principle in multivalley semiconductors such as Ge and Si.

[2)] Some of the material in Sec. 3 was published by us in an earlier communication.[8]

[1] A. S. Kaminskiĭ, Ya. E. Pokrovskiĭ, and N. V. Alkeev, Zh. Eksp. Teor. Fiz. 59, 1937 (1970) [Sov. Phys. JETP 32, 1048 (1971)].
[2] G. Kirczenow, Solid State Commun. 21, 713 (1977); Can. J. Phys. 55, 1787 (1977).
[3] S.-Y. J. Wang and C. Kittel, Phys. Lett. A 42, 189 (1972).
[4] M. L. W. Thewalt, Can. J. Phys. 55, 1463 (1977).
[5] R. R. Parsons, Solid State Commun. 22, 671 (1977).
[6] V. D. Kulakovskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. 27, 217 (1978) [JETP Lett. 27, 202 (1978)].
[7] A. S. Kaminskiĭ, V. A. Karasyuk, and Ya. E. Pokrovskiĭ, Zh. Eksp. Teor. Fiz. 74, 2234 (1978) [Sov. Phys. JETP 47, 1162 (1978)].
[8] V. D. Kulakovskiĭ, A. V. Malyavkin, and V. B. Timofeev, Pis'ma Zh. Eksp. Teor. Fiz. 27, 576 (1978) [JETP Lett. 27, 542 (1978)].
[9] W. Kohn, Solid State Phys., vol. 5, ed. F. Seitz, D. Trunbull, Academic Press, New York, 1957.
[10] J. M. Cherlow, R. L. Aggrawal, and B. Lax, Phys. Rev. B 7, 4547 (1973).
[11] R. Sauer and J. Weber, Phys. Rev. Lett. 36, 48 (1976).
[12] G. L. Bir and G. E. Pikus, Simmetriya i deformatsionnye éffekty v poluprovodnikakh (Symmetry and Deformation Effects in Semiconductors), Nauka, 1972.
[13] G. L. Bir and G. E. Pikus, Proc. Seventh Intern. Conf. on Physics of Semiconductors, Paris, 1964, Vol. 4, publ. by Dunod, Paris & Academic Press, New York (1966), p. 789.
[14] P. J. Dean, W. F. Flood, and G. Kaminsky, Phys. Rev. 163, 721 (1967).
[15] K. R. Elliott, G. C. Osborn, D. L. Smith, and T. C. McGill, Phys. Rev. B 17, 1808 (1978).
[16] P. D. Altukhov, K. N. El'tsov, G. E. Pikus, and A. A. Pogachev, Pis'ma Zh. Eksp. Teor. Fiz. 26, 468 (1977) [JETP Lett. 26, 337 (1977)].
[17] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics), Nauka, 1974 [Pergamon, 1976].
[18] H.-J. Wünsche, K. Henneberger, and V. E. Khartsiev, Phys. Status Solidi B 86, 505 (1978).
[19] D. K. Wilson and G. Feher, Phys. Rev. 124, 1068 (1961).
[20] F. Merlet, B. Pajot, Ph. Arcas, and A. M. Jean-Louis, Phys. Rev. B 12, 3297 (1975).

Translated by J. G. Adashko